Electronic Supplementary Information

**Ni**II-**Ln**III complexes with o-vanillin as main ligand: syntheses, structures, magnetic and magnetocaloric properties

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Figure S1. Molecular structure of 2 with atom numbering. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles: Ni-O1 2.007(2), Ni-O2 2.003(2), Ni-O5 2.005(2), Ni-O6 2.007(2), Ni-O7 2.076(2), Ni-O8 2.071(2), Ce-O1 2.423(2), Ce-O2 2.425(2), Ce-O3 2.629(2), Ce-O4 2.600(2), Ce-O9 2.615(2), Ce-O10 2.578(2), Ce-O12 2.612(2), Ce-O13 2.652(2), Ce-O15 2.571(2), Ce-O16 2.613(2) Å, O1 Ni O2 80.86(7), O1 Ce O2 64.88(6), Ni O1 Ce 107.07(7), Ni O2 Ce 107.17(7)°.
Figure S2. Molecular structure of 3 with atom numbering. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles: Ni-O1 1.997(2), Ni-O2 1.998(2), Ni-O4 2.005(2), Ni-O5 2.003(2), Ni-O7 2.079(3), Ni-O8 2.077(3), Tb-O1 2.353(2), Tb-O2 2.425(2), Tb-O3 2.543(2), Tb-O4 2.332(2), Tb-O10 2.435(3), Tb-O11 2.517(3), Tb-O13 2.507(2), Tb-O14 2.481(3), Tb-O16 2.487(3), Tb-O17 2.498(3) Å, O1 Ni O4 78.44(9), O1 Tb O4 65.38(7), Ni O1 Tb 107.82(9), Ni O2 Tb 108.31(9)°.
Figure S3. Field dependence of the magnetization for complex 4 at $T = 2$ K. The solid line corresponds to the best fit described in the text with $J_{\text{NiGd}} = 2.48$ cm$^{-1}$, $D_{\text{Ni}} = 4.7$ cm$^{-1}$ and $g = 2.05$.

Figure S4. Field dependence of the magnetization for complex 1 at $T = 2$ K. The solid line corresponds to the best fit described in the text with $J_{\text{NiGd}} = 2.77$ cm$^{-1}$, $D_{\text{Ni}} = 2.8$ cm$^{-1}$, $g = 2.03$, without the $zJ$ term.
Figure S5. Field dependence of the magnetization for complex 5 at \( T = 2\)–\( 10 \text{ K} \), step 1 K and 20 K. The solid lines correspond to the best fit described in the text with \( J_{\text{NiGd}} = 2.31 \text{ cm}^{-1} \), \( D_{\text{Ni}} = 0.7 \text{ cm}^{-1} \) and \( g = 2.04 \).

Figure S6. Field dependence of the magnetization for complex 7 at \( T = 2\)–\( 10 \text{ K} \), step 1 K. The solid lines correspond to the best fit described in the text with \( J_{\text{NiNi}} = 43.8 \text{ cm}^{-1} \), \( J_{\text{NiGd}} = 1.21 \text{ cm}^{-1} \), \( g = 2.06 \) and \( D_{\text{Ni}} = 5.8 \text{ cm}^{-1} \).
Figure S7. Field dependence of the magnetization for complex 8 at $T = 2$ K. The solid line corresponds to the best fit described in the text with $J_{\text{NiNi}} = 25.0$ cm$^{-1}$, $J_{\text{NiGd}} = 1.40$ cm$^{-1}$, $g = 2.00$, $D_{\text{Ni}} = 5.5$ cm$^{-1}$, without the $zJ$ term.

Figure S8. Field dependence of the magnetization for complex 9 at $T = 2$ K. The solid line corresponds to the best fit described in the text with $J_{\text{NiNi}} = 33.8$ cm$^{-1}$, $J_{\text{NiGd}} = 1.12$ cm$^{-1}$, $g = 2.01$ and $D_{\text{Ni}} = 5.5$ cm$^{-1}$.
Figure S9. Temperature dependence of the $\chi_M T$ product for complex 10. The solid line corresponds to $J_{\text{NiNi}} = 25.0$ cm$^{-1}$, $g = 2.22$ and $D_{\text{Ni}} = 5.4$ cm$^{-1}$.

Figure S10. Field dependence of the magnetization for complex 10 at $T = 2$ K. The solid line corresponds to the best fit described in the text with $J_{\text{NiNi}} = 25.0$ cm$^{-1}$, $g = 2.22$ and $D_{\text{Ni}} = 5.4$ cm$^{-1}$. 
Figure S11. From top to bottom (for complexes 1, 5 and 7, respectively): Temperature-dependence of the entropy normalized to the gas constant, $S/R$, for the indicated applied field changes. Dotted line is the non-magnetic lattice contribution to the entropy.